## *5.10 Tritium Geochemistry And $K_d$ Values*

### *5.10.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation*

Tritium, a radioactive isotope of hydrogen with a half life ($t_{½}$) of 12.3 y, readily combines with oxygen to form water. Its behavior in aqueous systems is controlled by hydrologic processes and it migrates at essentially the same velocity as surface- and groundwaters. Aqueous speciation, precipitation, and sorption processes are not expected to affect the mobility of tritium in soil/water systems.

### *5.10.2 General Geochemistry*

Tritium ($^3$H) is a radioactive isotope of hydrogen. Three isotopes of hydrogen are known. These include the 2 stable isotopes $^1$H (protium or H) and $^2$H (deuterium or D), and the radioactive isotope $^3$H (tritium or T). Tritium has a half life ($t_{½}$) of 12.3 y, and disintegrates into helium-3 ($^3$He) by emission of a weak beta ($\beta^-$) particle (Rhodehamel *et al.*, 1971). Tritium is formed by natural and man-made processes (Cotton and Wilkinson, 1980). Tritium is formed in the upper atmosphere mainly by the nuclear interaction of nitrogen with fast neutrons induced by cosmic ray reactions. The relative abundances of $^1$H, $^2$H, and $^3$H in natural water are 99.984, 0.016, and 0-$10^{-15}$ percent, respectively (Freeze and Cherry, 1979). Tritium can also be created in nuclear reactors as a result of processes such as thermal neutron reactions with $^6$Li.

As an isotope of hydrogen, tritium in soil systems behaves like hydrogen and will exist in ionic, gaseous, and liquid forms (*e.g.,* tritiated water, HTO). Ames and Rai (1978) discuss the geochemical behavior of tritium, and summarize field and laboratory studies of the mobility of tritium in soil systems. Because tritium readily combines with oxygen to form water, its behavior in aqueous systems is controlled by hydrologic processes. Because of these properties and its moderately long half life, tritium has been used as an environmental isotopic indicator to study hydrologic flow conditions. Rhodehamel *et al.* (1971) present an extensive bibliography (more than 1,200 references) and summarize the use of tritium in hydrologic studies through 1966. Tritium has been used to study recharge and pollution of groundwater reservoirs; permeability of aquifers; velocity, flow patterns, and stratification of surface- and groundwater bodies; dispersion and mixing processes in surface- and groundwaters; movement of soil moisture; chemisorption of soils and water-containing materials; biological uptake and release of water; and secondary recovery techniques for petroleum resources. IAEA (1979) published the proceedings from a 1978 conference dealing with the behavior of tritium in the environment. The conference was designed to provide information on the residence time and distribution of tritium in environmental systems and the incorporation of tritium into biological materials and its transfer along the food chain.

Tritium-contamination may include surface- and groundwater, soil, sediment, and air components at a site. Of the contaminated sites considered in EPA/DOE/NRC (1993), tritium contamination has been identified at 12 of the 45 Superfund National Priorities List (NPL) sites and 1 of the 38 NRC Site Decommissioning Site Plan (SDMP) sites.

### *5.10.3 Aqueous Speciation*

Because tritium oxidizes rapidly to form isotopic water, aqueous speciation reactions do not affect the mobility of tritium in soil/water systems.

### *5.10.4 Dissolution/Precipitation/Coprecipitation*

Neither precipitation or coprecipitation processes affect the mobility of tritium in soil/water systems.

### *5.10.5 Adsorption/Desorption*

Because tritium readily combines with oxygen to form water, its behavior in aqueous systems is controlled by hydrologic processes and it migrates at essentially the same velocity as surface and groundwaters. Sorption processes are therefore not expected to be important relative to the movement of tritium through aqueous environments. Typically, a partition coefficient, $K_d$, of 0 ml/g is used to model the migration of tritium in soil and groundwater environments. As an exception, Thibault *et al.* (1990), based on a review of published studies, list 0.04 to 0.1 ml/g as the range for $K_d$ values for tritium in sandy soils. Although tritium may substitute for hydrogen in water on clays and other hydrated soil constituents, Ames and Rai (1978) indicate that this reaction is not important relative to the mobility of tritium based on their review of published laboratory and field studies. Some laboratory studies considered in their review describe fixation of isotopic water on clays and other hydrated minerals, while others indicate minimal fixation. All field studies reviewed by Ames and Rai indicate that tritium migrates at the same velocity as surface- and groundwaters.

### *5.10.6 Partition Coefficient, $K_d$, Values*

A review of the literature pertaining to $K_d$ values for tritium was not conducted given the limited availability of $K_d$ values for tritium (see section above) and limited importance of sorption processes relative to the mobility of tritium in aqueous environments.

## *5.11 Uranium Geochemistry and $K_d$ Values*

### *5.11.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation*

In essentially all geologic environments, +4 and +6 are the most important oxidation states of uranium.

Uranium(VI) species dominate in oxidizing environments. Uranium(VI) retention by soils and rocks in alkaline conditions is poor because of the predominance of neutral or negatively charged species. An increase in $CO_2$ pressure in soil solutions reduces U(VI) adsorption by promoting the formation of poorly sorbing carbonate complexes. Uranium(IV) species dominate in reducing environments. Uranium(IV) tends to hydrolyze and form strong hydrolytic complexes. Uranium(IV) also tends to form sparingly soluble precipitates that commonly control U(IV) concentrations in groundwaters. Uranium(IV) forms strong complexes with naturally occurring organic materials. Thus, in areas where there are high concentrations of dissolved organic materials, U(IV)-organic complexes may increase U(IV) solubility. There are several ancillary environmental parameters affecting uranium migration. The most important of these parameters include redox status, pH, ligand (carbonate, fluoride, sulfate, phosphate, and dissolved carbon) concentrations, aluminum- and iron-oxide mineral concentrations, and uranium concentrations.

### *5.11.2 General Geochemistry*

Uranium (U) has 14 isotopes; the atomic masses of these isotopes range from 227 to 240. All uranium isotopes are radioactive. Naturally-occurring uranium typically contains 99.283 percent $^{238}U$, 0.711 percent $^{235}U$, and 0.0054 percent $^{234}U$ by weight. The half-lives of these isotopes are 4.51 x $10^9$ y, 7.1 x $10^8$ y, and 2.47 x $10^5$ y, respectively. Uranium can exist in the +3, +4, +5, and +6 oxidation states, of which the +4 and +6 states are the most common states found in the environment.

The mineralogy of uranium-containing minerals is described by Frondel (1958). Uranium in the +4 and +6 oxidation states exists in a variety of primary and secondary minerals. Important U(IV) minerals include uraninite ($UO_2$ through $UO_{2.25}$) and coffinite [$USiO_4$] (Frondel, 1958; Langmuir, 1978). Aqueous U(IV) is inclined to form sparingly soluble precipitates, adsorb strongly to mineral surfaces, and partition into organic matter, thereby reducing its mobility in groundwater. Important U(VI) minerals include carnotite [$(K_2(UO_2)_2(VO_4)_2$], schoepite ($UO_3{\cdot}2H_2O$), rutherfordine ($UO_2CO_3$), tyuyamunite [$Ca(UO_2)_2(VO_4)_2$], autunite [$Ca(UO_2)_2(PO_4)_2$], potassium autunite [$K_2(UO_2)_2(PO_4)_2$], and uranophane [$Ca(UO_2)_2(SiO_3OH)_2$] (Frondel, 1958; Langmuir, 1978). Some of these are secondary phases which may form when sufficient uranium is leached from contaminated wastes or a disposal system and migrates downstream. Uranium is also found in phosphate rock and lignite[1] at concentrations that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, uranium enrichment is believed to be the result of uranium reduction to form insoluble precipitates, such as uraninite.

Contamination includes airborne particulates, uranium-containing soils, and uranium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by $^{234}U$, $^{235}U$, and/or $^{238}U$ has been identified at 35 of the 45 Superfund

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[1] Lignite is a coal that is intermediate in coalification between peat and subbituminous coal.

National Priorities List (NPL) sites and 26 of the 38 NRC Site Decommissioning Site Plan (SDMP) sites.

### 5.11.3 Aqueous Speciation

Because of its importance in nuclear chemistry and technology, a great deal is known about the aqueous chemistry of uranium [reviewed by Baes and Mesmer (1976), Langmuir (1978), and Wanner and Forest (1992)]. Uranium can exist in the +3, +4, +5, and +6, oxidation states in aqueous environments. Dissolved U(III) easily oxidizes to U(IV) under most reducing conditions found in nature. The U(V) aqueous species ($UO_2^+$) readily disproportionates to U(IV) and U(VI).[1] Consequently, U(IV) and U(VI) are the most common oxidation states of uranium in nature. Uranium will exist in the +6 and +4 oxidation states, respectively, in oxidizing and more reducing environments.

Both uranium species, $UO_2^{2+}$ and $U^{4+}$, hydrolyze readily. The $U^{4+}$ ion is more readily hydrolyzed than $UO_2^{2+}$, as would be expected from its higher ionic charge. Langmuir (1978) calculated U(IV) speciation in a system containing typical natural water concentrations of chloride (10 mg/l), fluoride (0.2 mg/l), phosphate (0.1 mg/l), and sulfate (100 mg/l). Below pH 3, $UF_2^{2+}$ was the dominant uranium species. The speciation of dissolved U(IV) at pH values greater than 3 is dominated by hydrolytic species such as $U(OH)_3^+$ and $U(OH)_4^N$(aq). Complexes with chloride, fluoride, phosphate, and sulfate were not important above pH 3. The total U(IV) concentration in solution is generally quite low, between 3 and 30 µg/l, because of the low solubility of U(IV) solid phases (Bruno *et al.*, 1988; Bruno *et al.*, 1991). Precipitation is discussed further in the next section.

Dissolved U(VI) hydrolyses to form a number of aqueous complexes. The distribution of U(VI) species is presented in Figures 5.6a-b and 5.7. The distribution of uranyl hydrolytic species (Figures 5.6a-b) was calculated as a function of pH using the MINTEQA2 code. The U(VI) aqueous species included in the speciation calculations are listed in Table 5.16. The thermodynamic data for these aqueous species were taken primarily from Wanner and Forest (1992). Because dissolved uranyl ions can be present as polynuclear[2] hydroxyl complexes, the hydrolysis of uranyl ions under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations of total dissolved uranium, 0.1 and 1,000 µg/l, were used in these calculations. Hem (1985, p. 148) gives 0.1 to 10 µg/l as the range for dissolved uranium in

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[1] Disproportionation is defined in the glossary at the end of this letter report. This particular disproportionation reaction can be described as:

$$2UO_2^+ + 4H_3O^+ = UO_2^{2+} + U^{4+}.$$

[2] A polynuclear species contains more than 1 central cation moiety, *e.g.*, $(UO_2)_2CO_3(OH)_3^-$ and $Pb_4(OH)_4^{4+}$.

most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 µg/l.

In a U(VI)-water system, the dominant species were $UO_2^{2+}$ at pH values less than 5, $UO_2(OH)_2^{\circ}$ (aq) at pH values between 5 and 9, and $UO_2(OH)_3^-$ at pH values between 9 and 10. This was true for both uranium concentrations, 0.1 µg/l (Figure 5.6a) and 1,000 µg/l dissolved U(VI) (Figure 5.6b). At 1,000 µg/l dissolved uranium, some polynuclear species, $(UO_2)_3(OH)_5^+$ and $(UO_2)_2(OH)_2^{2+}$, were calculated to exist between pH 5 and 6. Morris *et al.* (1994) using spectroscopic techniques provided additional proof that an increasing number of polynuclear species were formed in systems containing higher concentrations of dissolved uranium.

A large number of additional uranyl species (Figure 5.7) are likely to exist in the chemically more complicated system such as the water composition in Table 5.1 and 1,000 µg/l dissolved U(VI). At pH values less than 5, the $UO_2F^+$ species dominates the system, whereas at pH values greater than 5, carbonate complexes [$UO_2CO_3^{\circ}$(aq), $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$] dominate the system. These calculations clearly show the importance of carbonate chemistry on U(VI) speciation. For this water composition, complexes with chloride, sulfate, and phosphate were relatively less important. Consistent with the results in Figure 5.7, Langmuir (1978) concluded that the uranyl complexes with chloride, phosphate, and sulfate were not important in a typical groundwater. The species distribution illustrated in Figure 5.7 changes slightly at pH values greater than 6 if the concentration of total dissolved uranium is decreased from 1,000 to 1 µg/l. At the lower concentration of dissolved uranium, the species $(UO_2)_2CO_3(OH)_3^-$ is no longer present as a dominant aqueous species.

Sandino and Bruno (1992) showed that $UO_2^{2+}$-phosphate complexes [$UO_2HPO_4^{\circ}$(aq) and $UO_2PO_4^-$] could be important in aqueous systems with a pH between 6 and 9 when the total concentration ratio $PO_4$(total)/$CO_3$(total) is greater than 0.1. Complexes with sulfate, fluoride, and possibly chloride are potentially important uranyl species where concentrations of these anions are high. However, their stability is considerably less than the carbonate and phosphate complexes (Wanner and Forest, 1992).

Organic complexes may also be important to uranium aqueous chemistry. The uncomplexed uranyl ion has a greater tendency to form complexes with fulvic and humic acids than many other metals with a +2 valence (Kim, 1986). This has been attributed to the greater "effective charge" of the uranyl ion compared to other divalent metals. The effective charge has been estimated to be about +3.3 for U(VI) in $UO_2^{2+}$. Kim (1986) concluded that, in general, +6 actinides, including U(VI), would have approximately the same tendency to form humic- or fulvic-acid complexes as to hydrolyze or form carbonate complexes. This suggests that the dominant reaction with the uranyl ion that will take place in a groundwater will depend largely on the relative concentrations of hydroxide, carbonate, and organic material concentrations. He also concluded, based on comparison of stability constants, that the tendency for $U^{4+}$ to form humic- or fulvic-acid complexes is less than its tendency to hydrolyze or form carbonate complexes. Importantly, U(IV) and U(VI) can form stable organic complexes, thereby increasing their solubility and mobility.

**Table 5.16.** Uranium(VI) aqueous species included in the speciation calculations.

| **Aqueous Species** |
|---|
| $UO_2^{2+}$, $UO_2OH^+$, $UO_2(OH)_2^{N}$(aq), $UO_2(OH)_3^-$, , $UO_2(OH)_4^{2-}$,<br>$(UO_2)_2OH^{3+}$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$,<br>$(UO_2)_3(OH)_7^-$, $(UO_2)_4(OH)_7^+$, $U_6(OH)_{15}^{9+}$ |
| $UO_2CO_3^{N}$(aq), $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_3^{5-}$,<br>$(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$, $(UO_2)_2CO_3(OH)_3^-$ |
| $UO_2PO_4^-$, $UO_2HPO_4^{N}$(aq), $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$,<br>$UO_2(H_2PO_4)_2^{N}$(aq), $UO_2(H_2PO_4)(H_3PO_4)^+$, |
| $UO_2SO_4^{N}$(aq), $UO_2(SO_4)_2^{2-}$ |
| $UO_2NO_3^+$ |
| $UO_2Cl^+$, $UO_2Cl_2^{N}$(aq), $UO_2F^+$, $UO_2F_2^{N}$(aq), $UO_2F_3^-$, $UO_2F_4^{2-}$ |
| $UO_2SiO(OH)_3^+$ |

### *5.11.4 Dissolution/Precipitation/Coprecipitation*

Dissolution, precipitation, and coprecipitation have a much greater effect on the concentrations of U(IV) than on the concentration of U(VI) in groundwaters. In most cases, these processes will likely not control the concentration of U(VI) in oxygenated groundwaters far from a uranium source. Near a uranium source, or in reduced environments, these processes tend to become increasingly important and several (co)precipitates may form depending on the environmental conditions (Falck, 1991; Frondel, 1958). Reducing conditions may exist in deep aquifers, marsh areas, or engineered barriers that may cause U(IV) to precipitate. Important U(IV) minerals include uraninite (compositions ranging from $UO_2$ to $UO_{2.25}$), coffinite ($USiO_4$), and ningyoite [$CaU(PO_4)_2{\cdot}2H_2O$] (Frondel, 1958; Langmuir, 1978). Important U(VI) minerals include carnotite [($K_2(UO_2)_2(VO_4)_2$], schoepite ($UO_3{\cdot}2H_2O$), rutherfordine ($UO_2CO_3$), tyuyamunite [$Ca(UO_2)_2(VO_4)_2$], autunite [$Ca(UO_2)_2(PO_4)_2$], potassium autunite [$K_2(UO_2)_2(PO_4)_2$], and uranophane [$Ca(UO_2)_2(SiO_3OH)_2$] (Frondel, 1958; Langmuir, 1978). Carnotite, a U(VI) mineral, is found in the oxidized zones of uranium ore deposits and uraninite, a

U(IV) mineral, is a primary mineral in reducing ore zones (Frondel, 1958). The best way to model the concentration of precipitated uranium is not with the $K_d$ construct, but through the use of solubility constants.

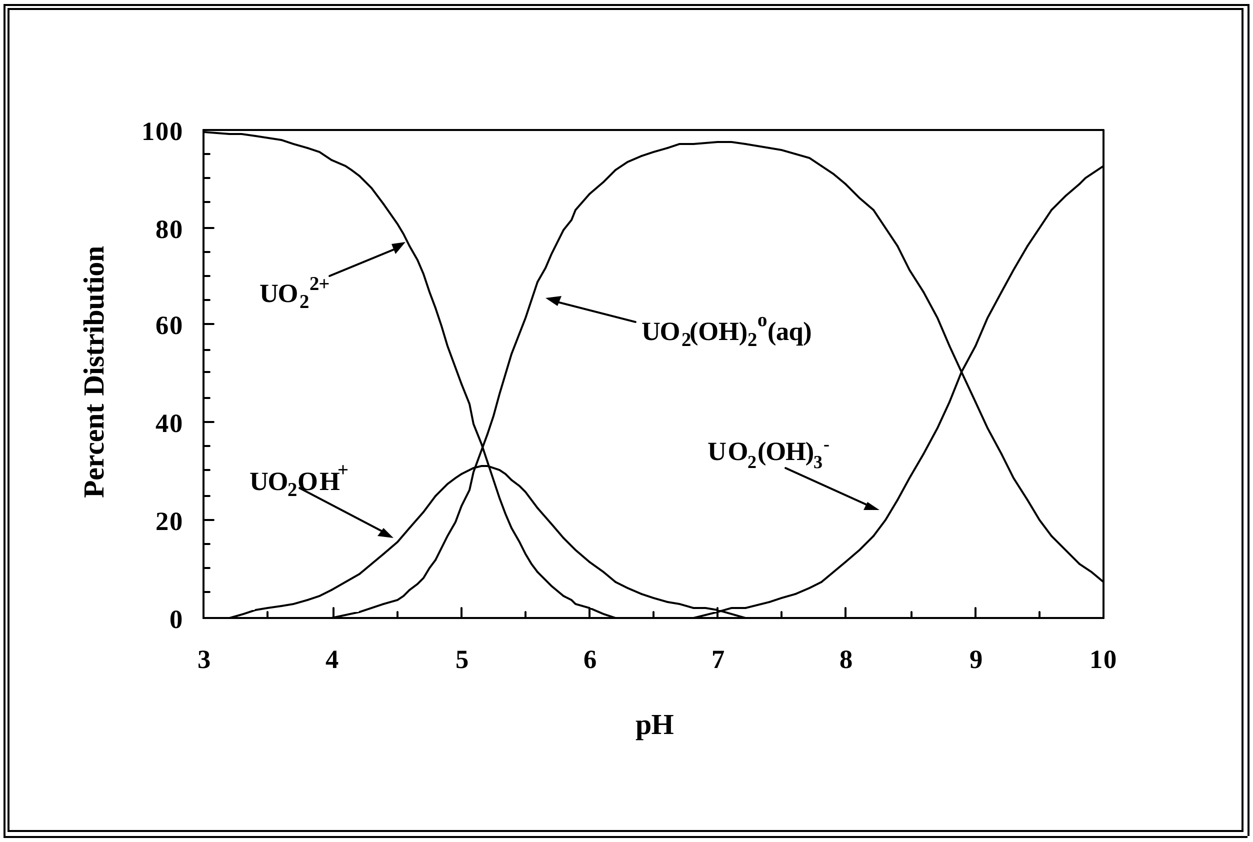

**Figure 5.6a**. Calculated distribution of U(VI) hydrolytic species as a function of pH at 0.1 µg/l total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water (*i.e.*, absence of complexing ligands other than $OH^-$) and thermodynamic data from Wanner and Forest (1992).]

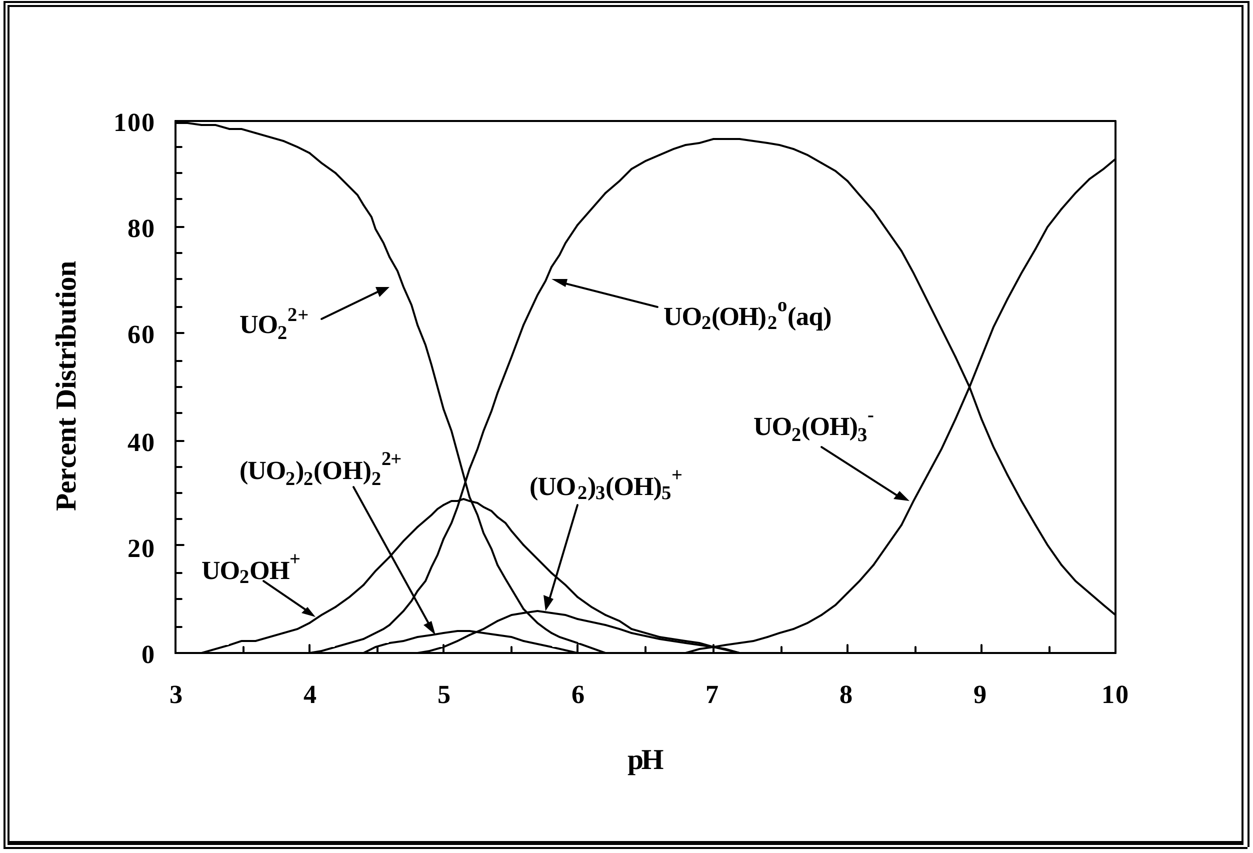

**Figure 5.6b**. Calculated distribution of U(VI) hydrolytic species as a function of pH at 1,000 µg/l total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water and thermodynamic data from Wanner and Forest (1992).]

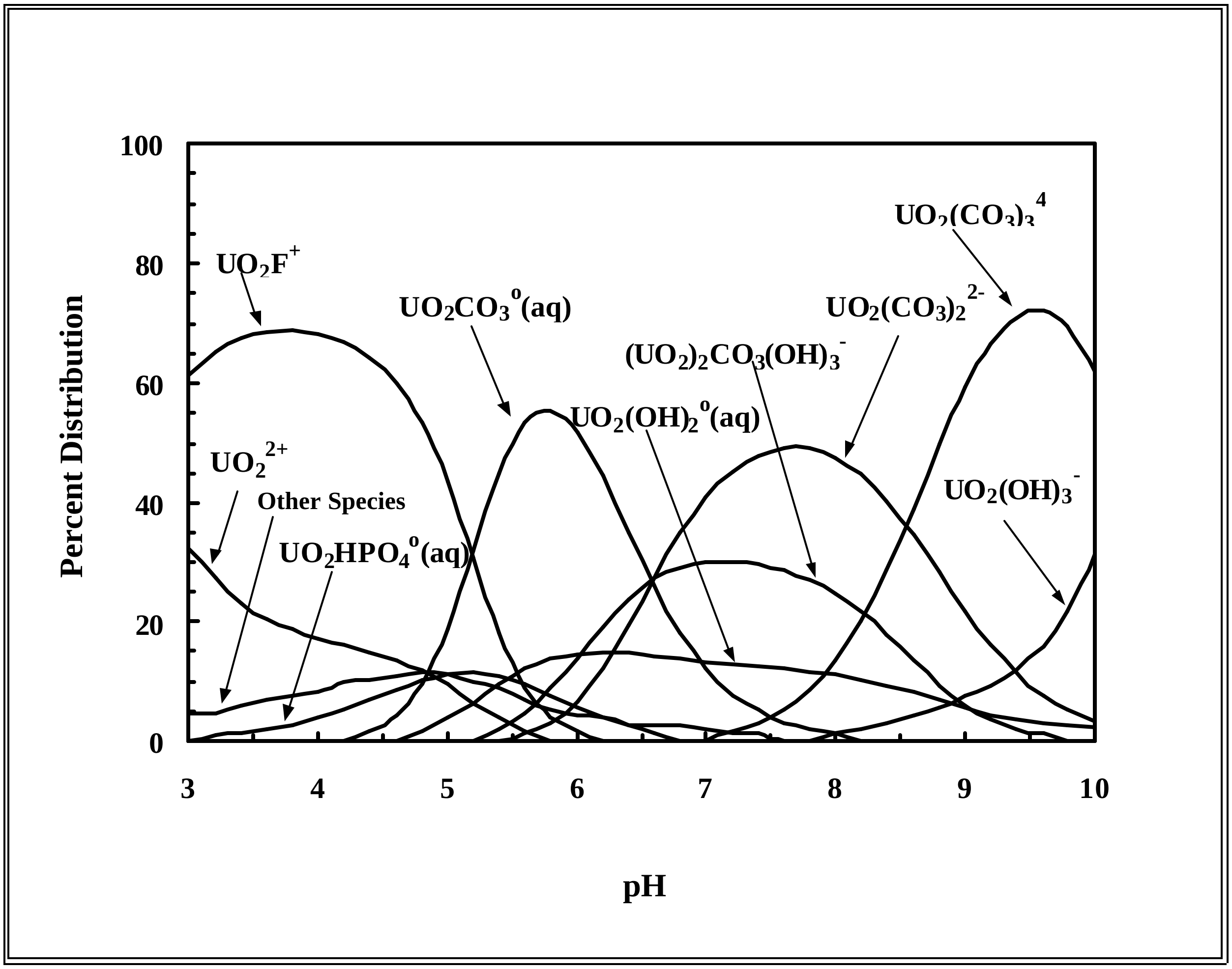

**Figure 5.7**. Calculated distribution of U(VI) aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1,000 µg/l total dissolved U(VI) and thermodynamic data from Wanner and Forest (1992).]

### *5.11.5 Sorption/Desorption*

In low ionic strength solutions with low U(VI) concentrations, dissolved uranyl concentrations will likely be controlled by cation exchange and adsorption processes. The uranyl ion and its complexes adsorb onto clays (Ames *et al.*, 1982; Chisholm-Brause *et al.*, 1994), organics (Borovec *et al.*, 1979; Read *et al.*, 1993; Shanbhag and Choppin, 1981), and oxides (Hsi and Langmuir, 1985; Waite *et al.*, 1994). As the ionic strength of an oxidized solution increases, other ions, notably $Ca^{2+}$, $Mg^{2+}$, and $K^+$, will displace the uranyl ion from soil exchange sites, forcing it into solution. For this reason, the uranyl ion is particularly mobile in high ionic-strength solutions. Not only will other cations dominate over the uranyl ion in competition for exchange sites, but carbonate ions will form strong soluble complexes with the uranyl ion, further lowering the activity of this ion while increasing the total amount of uranium in solution (Yeh and Tripathi, 1991).

Some of the sorption processes to which uranyl ion is subjected are not completely reversible. Sorption onto iron and manganese oxides can be a major process for extraction of uranium from solution (Hsi and Langmuir, 1985; Waite *et al.*, 1994). These oxide phases act as a somewhat irreversible sink for uranium in soils. Uranium bound in these phases is not generally in isotopic equilibrium with dissolved uranium in the same system, suggesting that the reaction rate mediating the transfer of the metal between the 2 phases is slow.

Naturally occurring organic matter is another possible sink for U(VI) in soils and sediments. The mechanisms by which uranium is sequestered by organic matter have not been worked out in detail. One possible process involves adsorption of uranium to humic substances through rapid ion-exchange and complexation processes with carboxylic and other acidic functional groups (Boggs *et al.*, 1985; Borovec *et al.*, 1979; Idiz *et al.*, 1986; Shanbhag and Choppin, 1981; Szalay, 1964). These groups can coordinate with the uranyl ion, displacing waters of hydration, to form stable complexes. A process such as this probably accounts for a significant fraction of the organically bound uranium in surface and subsurface soils. Alternatively, sedimentary organics may act to reduce dissolved U(VI) species to U(IV) (Nash *et al.*, 1981).

Uranium sorption to iron oxide minerals and smectite clay has been shown to be extensive in the absence of dissolved carbonate (Ames *et al.*, 1982; Hsi and Langmuir, 1985; Kent *et al.*, 1988). However, in the presence of carbonate and organic complexants, sorption has been shown to be substantially reduced or severely inhibited (Hsi and Langmuir, 1985; Kent *et al.*, 1988).

Aqueous pH is likely to have a profound effect on U(VI) sorption to solids. There are 2 processes by which it influences sorption. First, it has a great impact on uranium speciation (Figures 5.6a-b and 5.7) such that poorer-adsorbing uranium species will likely exist at pH values between about 6.5 and 10. Secondly, decreases in pH reduce the number of exchange sites on variable charged surfaces, such as iron-, aluminum-oxides, and natural organic matter.

### **5.11.6 Partition Coefficient, $K_d$, Values**

#### *5.11.6.1 General Availability of $K_d$ Values*

More than 20 references (Appendix J) that reported $K_d$ values for the sorption of uranium onto soils, crushed rock material, and single mineral phases were identified during this review.[1] These studies were typically conducted to support uranium migration investigations and safety assessments associated with the genesis of uranium ore deposits, remediation of uranium mill tailings, agriculture practices, and the near-surface and deep geologic disposal of low-level and high-level radioactive wastes (including spent nuclear fuel). These studies indicated that pH and dissolved carbonate concentrations are the 2 most important factors influencing the adsorption behavior of U(VI).

The uranium $K_d$ values listed in Appendix J exhibit large scatter. This scatter increases from approximately 3 orders of magnitude at pH values below pH 5, to approximately 3 to 4 orders of magnitude from pH 5 to 7, and approximately 4 to 5 orders of magnitude at pH values from pH 7 to 9. At the lowest and highest pH regions, it should be noted that 1 to 2 orders of the observed variability actually represent uranium $K_d$ values that are less than 10 ml/g. At pH values less than 3.5 and greater than 8, this variability includes $K_d$ values of less than 1 ml/g.

Uranium $K_d$ values show a trend as a function of pH. In general, the adsorption of uranium by soils and single-mineral phases in carbonate-containing aqueous solutions is low at pH values less than 3, increases rapidly with increasing pH from pH 3 to 5, reaches a maximum in adsorption in the pH range from pH 5 to 8, and then decreases with increasing pH at pH values greater than 8. This trend is similar to the *in situ* $K_d$ values reported by Serkiz and Johnson (1994), and percent adsorption values measured for uranium on single mineral phases such as those reported for iron oxides (Hsi and Langmuir, 1985; Tripathi, 1984; Waite *et al.*, 1992, 1994), clays (McKinley *et al.*, 1995; Turner *et al.*, 1996; Waite *et al.*, 1992), and quartz (Waite *et al.*, 1992). This pH-dependent behavior is related to the pH-dependent surface charge properties of the soil minerals and complex aqueous speciation of dissolved U(VI), especially near and above neutral pH conditions where dissolved U(VI) forms strong anionic uranyl-carbonato complexes with dissolved carbonate.

#### *5.11.6.2 Look-Up Table*

Solution pH was used as the basis for generating a look-up table for the range of estimated minimum and maximum $K_d$ values for uranium. Given the orders of magnitude variability observed for reported uranium $K_d$ values, a subjective approach was used to estimate the minimum and maximum $K_d$ values for uranium as a function of pH. These values are listed in Table 5.17. For $K_d$ values at non-integer pH values, especially given the rapid changes in uranium adsorption observed at pH values less than 5 and greater than 8, the reader should assume a linear relationship between each adjacent pair of pH-$K_d$ values listed in Table 5.17.

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[1] Since the completion of our review and analysis of $K_d$ data for the selected contaminants and radionuclides, the studies by Pabalan *et al.* (1998), Payne *et al.* (1998), Redden *et al.* (1998), Rosentreter *et al.* (1998), and Thompson *et al.* (1998) were identified and may be of interest to the reader.

**Table 5.17.** Look-up table for estimated range of $K_d$ values for uranium based on pH.

| **$K_d$ (ml/g)** | **pH** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
| Minimum | <1 | 0.4 | 25 | 100 | 63 | 0.4 | <1 | <1 |
| Maximum | 32 | 5,000 | 160,000 | 1,000,000 | 630,000 | 250,000 | 7,900 | 5 |

The boundary representing the minimum limit for uranium $K_d$ values is based on values calculated for quartz from data given in Waite *et al.* (1992) and the $K_d$ values reported by Kaplan *et al.* (1996, 1998), Lindenmeirer *et al.* (1995), and Serne *et al.* (1993). It is unlikely that actual $K_d$ values for U(VI) can be much lower than those represented by this lower boundary. At the pH extremes along this curve, the uranium $K_d$ values are very small. Moreover, if one considers potential sources of error resulting from experimental methods, it is difficult to rationalize uranium $K_d$ values much lower than this lower boundary.

The curve representing the maximum limit for uranium $K_d$ values is based on $K_d$ values calculated for ferrihydrite and kaolinite from data given in Waite *et al.* (1992). It is estimated that this maximum limit is biased high, possibly by an order of magnitude or more especially at pH values greater than 5. This estimate is partially based on the distribution of measured $K_d$ values listed in Appendix J, and the assumption that some of the very large $K_d$ measurements may have included precipitation of uranium-containing solids due to starting uranium solutions being oversaturated. Moreover, measurements of uranium adsorption onto crushed rock materials may include U(VI)/U(IV) redox/precipitation reactions resulting from contact of dissolved U(VI) with Fe(II) exposed on the fresh mineral surfaces.

#### 5.11.6.2.1 Limits of $K_d$ Values with Respect to Dissolved Carbonate Concentrations

As noted in several studies summarized in Appendix J and in surface complexation studies of uranium adsorption by Tripathi (1984), Hsi and Langmuir (1985), Waite *et al.* (1992, 1994), McKinley *et al.* (1995), Duff and Amrheim (1996), Turner *et al.* (1996), and others, dissolved carbonate has a significant effect on the aqueous chemistry and solubility of dissolved U(VI) through the formation of strong anionic carbonato complexes. In turn, this complexation affects the adsorption behavior of U(VI) at alkaline pH conditions.

No attempt was made to statistically fit the $K_d$ values summarized in Appendix J as a function of dissolved carbonate concentrations. Typically carbonate concentrations were not reported and/or discussed, and one would have to make assumptions about possible equilibrium between the solutions and atmospheric or soil-related partial pressures of $CO_2$ or carbonate phases present in the soil samples. Given the complexity of these reaction processes, it is recommended that the reader consider the application of geochemical reaction codes, and surface complexation models in particular, as the best approach to predicting the role of dissolved carbonate in the adsorption behavior of uranium and derivation of U(VI) $K_d$ values when site-specific $K_d$ values are not available.

#### 5.11.6.2.2 Limits of $K_d$ Values with Respect to Clay Content and CEC

No attempt was made to statistically fit the $K_d$ values summarized in Appendix J as a function of clay content or CEC. The extent of clay content and CEC data, as noted from information compiled during this review, is limited to a few studies that cover somewhat limited geochemical conditions. Moreover, Serkiz and Johnson (1994) found no correlation between their uranium *in situ* $K_d$ values and the clay content or CEC of their soils. Their systems covered the pH conditions from 3 to 7.

However, clays have an important role in the adsorption of uranium in soils. Attempts have been made (*e.g.*, Borovec, 1981) to represent this functionality with a mathematical expression, but such studies are typically for limited geochemical conditions. Based on studies by Chisholm-Brause (1994), Morris *et al.* (1994), McKinley *et al.* (1995), Turner *et al.* (1996), and others, uranium adsorption onto clay minerals is complicated and involves multiple binding sites, including exchange and edge-coordination sites. The reader is referred to these references for a detailed treatment of the uranium adsorption on smectite clays and application of surface complexation modeling techniques for such minerals.

#### 5.11.6.2.3 Use of Surface Complexation Models to Predict Uranium $K_d$ Values

As discussed in Chapter 4 and in greater detail in Volume I of this report, electrostatic surface complexation models (SCMs) incorporated into chemical reaction codes, such as EPA's MINTEQA2, may be used to predict the adsorption behavior of some radionuclides and other metals and to derive $K_d$ values as a function of key geochemical parameters, such as pH and carbonate concentrations. Typically, the application of surface complexation models is limited by the availability of surface complexation constants for the constituents of interest and competing ions that influence their adsorption behavior.

The current state of knowledge regarding surface complexation constants for uranium adsorption onto important soil minerals, such as iron oxides, and development of a mechanistic understanding of these reactions is probably as advanced as those for any other trace metal. In the absence of site-specific $K_d$

values for the geochemical conditions of interest, the reader is encouraged to apply this technology to predict bounding uranium $K_d$ values and their functionality with respect to important geochemical parameters.

### *5.12 Conclusions*

One objective of this report is to provide a "thumb-nail sketch" of the geochemistry of cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium, and uranium. These contaminants represent 6 nonexclusive contaminant categories: cations, anions, radionuclides, non-attenuated contaminants, attenuated contaminants, and redox-sensitive contaminants (Table 5.18). By categorizing the contaminants in this manner, general geochemical behaviors of 1 contaminant may be extrapolated by analogy to other contaminants in the same category. For example, anions, such as $NO_3^-$ and $Cl^-$, commonly adsorb to geological materials to a limited extent. This is also the case observed for the sorption behavior of anionic Cr(VI).

Important solution speciation, (co)precipitation/dissolution, and adsorption reactions were discussed for each contaminant. The species distributions for each contaminant were calculated using the chemical equilibria code MINTEQA2 (Version 3.11, Allison *et al.*, 1991) for the water composition described in Tables 5.1 and 5.2. The purpose of these calculations was to illustrate the types of aqueous species that might exist in a groundwater. A summary of the results of these calculations are presented in Table 5.19. The speciation of cesium, radon, strontium, and tritium does not change between the pH range of 3 and 10; they exist as $Cs^+$, $Rn^0$, $Sr^{2+}$, and HTO, respectively (Ames and Rai, 1978; Rai and Zachara, 1984). Chromium (as chromate, $CrO_4^{2-}$), cadmium, and thorium have 2 or 3 different species across this pH range. Lead, plutonium, and uranium have several species. Calculations show that lead forms a large number of stable complexes. The aqueous speciation of plutonium is especially complicated because it may exist in groundwaters in multiple oxidation states [Pu(III), Pu(IV), Pu(V), and Pu(VI)] and it forms stable complexes with a large number of ligands. Because of redox sensitivity, the speciation of uranium exhibits a large number of stable complexes. Uranium(VI) also forms polynuclear complex species [complexes containing more than 1 mole of uranyl [*e.g.*, $(UO_2)_2CO_3OH^-$].

One general conclusion that can be made from the results in Table 5.19 is that, as the pH increases, the aqueous complexes tend to become increasingly more negatively charged. For example, lead, plutonium, thorium, and uranium are cationic at pH 3. At pH values greater than 7, they exist predominantly as either neutral or anionic species. Negatively charged complexes tend to adsorb less to soils than their respective cationic species. This rule-of-thumb stems from the fact that most minerals in soils have a net negative charge. Conversely, the solubility of several of these contaminants decreases dramatically as pH increases. Therefore, the net contaminant concentration in solution does not necessarily increase as the dominant aqueous species becomes more negatively charged.

**Table 5.18.** Selected chemical and transport properties of the contaminants.

| Element | Radio-nuclide[1] | Primary Species at pH 7 and Oxidizing Conditions | | | Redox Sensitive[2] | Transport Through Soils at pH 7 | |
|---|---|---|---|---|---|---|---|
| | | Cationic | Anionic | Neutral | | Not Retarded[3] | Retarded[3] |
| Cd | | x | | | x | | x |
| Cs | x | x | | | | | x |
| Cr | | | x | | x | x | x |
| Pb | | x | x | | x | | x |
| Pu | x | | x | x | x | | x |
| Rn | x | | | x | | x | |
| Sr | x | x | | | | | x |
| Th | x | | x | | | | x |
| $^{3}$H | x | | | x | | x | |
| U | x | | x | x | x | | x |

[1] Contaminants that are primarily a health concern as a result of their radioactivity are identified in this column. Some of these contaminants also exist as stable isotopes (*e.g.*, cesium and strontium).

[2] The redox status column identifies contaminants (Cr, Pu, and U) that have variable oxidation states within the pH and Eh limits commonly found in the environment and contaminants (Cd and Pb) whose transport is affected by aqueous complexes or precipitates involving other redox-sensitive constituents (*e.g.*, dissolved sulfide).

[3] Retarded or attenuated (nonconservative) transport means that the contaminant moves slower than water through geologic material. Nonretarded or nonattenuated (conservative) transport means that the contaminant moves at the same rate as water.

**Table 5.19**. Distribution of dominant contaminant species at 3 pH values for an oxidizing water described in Tables 5.1 and 5.2.[1]

| Element | pH 3 | | pH 7 | | pH 10 | |
|---|---|---|---|---|---|---|
| | Species | % | Species | % | Species | % |
| Cd | $Cd^{2+}$ | 97 | $Cd^{2+}$<br>$CdHCO_3^+$<br>$CdCO_3^{''}$(aq) | 84<br>6<br>6 | $CdCO_3^{''}$(aq) | 96 |
| Cs | $Cs^+$ | 100 | $Cs^+$ | 100 | $Cs^+$ | 100 |
| Cr | $HCrO_4^-$ | 99 | $CrO_4^{2-}$<br>$HCrO_4^-$ | 78<br>22 | $CrO_4^{2-}$ | 99 |
| Pb | $Pb^{2+}$<br>$PbSO_4^{''}$(aq) | 96<br>4 | $PbCO_3^{''}$(aq)<br>$Pb^{2+}$<br>$PbHCO_3^+$<br>$PbOH^+$ | 75<br>15<br>7<br>3 | $PbCO_3^{''}$(aq)<br>$Pb(CO_3)_2^{2-}$<br>$Pb(OH)_2^{''}$(aq)<br>$Pb(OH)^+$ | 50<br>38<br>9<br>3 |
| Pu | $PuF_2^{2+}$<br>$PuO_2^+$<br>$Pu^{3+}$ | 69<br>24<br>5 | $Pu(OH)_2(CO_3)_2^{2-}$<br>$Pu(OH)_4^{''}$(aq) | 94<br>5 | $Pu(OH)_2(CO_3)_2^{2-}$<br>$Pu(OH)_4^{''}$(aq) | 90<br>10 |
| Rn | $Rn^0$ | 100 | $Rn^0$ | 100 | $Rn^0$ | 100 |
| Sr | $Sr^{2+}$ | 99 | $Sr^{2+}$ | 99 | $Sr^{2+}$<br>$SrCO_3^{''}$(aq) | 86<br>12 |
| Th | $ThF_2^{2+}$<br>$ThF_3^+$ | 54<br>42 | $Th(HPO_4)_3^{2-}$<br>$Th(OH)_3CO_3^-$ | 76<br>22 | $Th(OH)_3CO_3^-$ | 99 |
| $^3H$ | HTO | 100 | HTO | 100 | HTO | 100 |
| U<br>0.1 µg/l | $UO_2F^+$<br>$UO_2^{2+}$<br>$UO_2F_2^{''}$(aq) | 62<br>31<br>4 | $UO_2(CO_3)_2^{2-}$<br>$UO_2(OH)_2^{''}$(aq)<br>$UO_2CO_3^{''}$(aq)<br>$UO_2PO_4^-$ | 58<br>19<br>17<br>3 | $UO_2(CO_3)_3^{4-}$<br>$UO_2(OH)_3^-$<br>$UO_2(CO_3)_2^{2-}$ | 63<br>31<br>4 |
| U<br>1,000 µg/l | $UO_2F^+$<br>$UO_2^{2+}$<br>$UO_2F_2^{''}$(aq) | 61<br>33<br>4 | $UO_2(CO_3)_2^{2-}$<br>$(UO_2)_2CO_3(OH)_3^-$<br>$UO_2(OH)_2^{''}$(aq)<br>$UO_2CO_3^{''}$(aq) | 41<br>30<br>13<br>12 | $UO_2(CO_3)_3^{4-}$<br>$UO_2(OH)_3^-$<br>$UO_2(CO_3)_2^{2-}$ | 62<br>32<br>4 |

[1] Only species comprising 3 percent or more of the total contaminant distribution are presented. Hence, the total of the percent distributions presented in table will not always equal 100 percent.

Another objective of this report is to identify the important chemical, physical, and mineralogical characteristics controlling sorption of these contaminants. These key aqueous- and solid-phase parameters were used to assist in the selection of appropriate minimum and maximum $K_d$ values. There are several aqueous- and solid-phase characteristics that can influence contaminant sorption. These characteristics commonly have an interactive effect on contaminant sorption, such that the effect of 1 parameter on sorption varies as the magnitude of other parameters changes. A list of some of the more important chemical, physical, and mineralogical characteristics affecting contaminant sorption are listed in Table 5.20.

Sorption of all the contaminants, except tritium and radon, included in this study is influenced to some degree by pH. The effect of pH on both adsorption and (co)precipitation is pervasive. The pH, per se, typically has a small direct effect on contaminant adsorption. However, it has a profound effect on a number of aqueous and solid phase properties that in turn have a direct effect on contaminant sorption. The effects of pH on sorption are discussed in greater detail in Volume I. As discussed above, pH has a profound effect on aqueous speciation (Table 5.19), which may affect adsorption. Additionally, pH affects the number of adsorption sites on variable-charged minerals (aluminum- and iron-oxide minerals), partitioning of contaminants to organic matter, CEC, formation of polynuclear complexes, oxidation state of contaminants and complexing/precipitating ligands, and $H^+$-competition for adsorption sites.

The redox status of a system also influences the sorption of several contaminants included in this study (Table 5.20). Like pH, redox has direct and indirect effects on contaminant (co)precipitation. The direct effect occurs with contaminants like uranium and chromium where the oxidized species form more soluble solid phases than the reduced species. Redox conditions also have a direct effect on the sorption of plutonium, but the effects are quite complicated. The indirect effects occur when the contaminants adsorb to redox sensitive solid phases or precipitate with redox sensitive ligands. An example of the former involves the reductive dissolution of ferric oxide minerals, which can adsorb (complex) metals strongly. As the ferric oxide minerals dissolve, the adsorption potential of the soil is decreased. Another indirect effect of redox on contaminant sorption involves sulfur-ligand chemistry. Under reducing conditions, S(VI) ($SO_4^{2-}$, sulfate) will convert into S(II) ($S^{2-}$, sulfide) and then the S(II) may form sparingly soluble cadmium and lead precipitates. Thus, these 2 redox sensitive reactions may have off-setting net effects on total contaminant sorption (sulfide precipitates may sequester some of the contaminants previously bound to ferric oxides).

Unlike most ancillary parameters, the effect of redox on sorption can be quite dramatic. If the bulk redox potential of a soil/water system is above the potential of the specific element redox reaction, the oxidized form of the redox sensitive element will exist. Below this critical value, the reduced form of the element will exist. Such a change in redox state can alter $K_d$ values by several orders of magnitude (Ames and Rai, 1978; Rai and Zachara, 1984).

**Table 5.20**. Some of the more important aqueous- and solid-phase parameters affecting contaminant sorption.[1]

| Element | Important Aqueous- and Solid-Phase Parameters Influencing Contaminant Sorption[2] |
|---|---|
| Cd | [Aluminum/Iron-Oxide Minerals], [Calcium], Cation Exchange Capacity, [Clay Mineral], [Magnesium], [Organic Matter], pH, Redox, [Sulfide] |
| Cs | [Aluminum/Iron-Oxide Minerals], [Ammonium], Cation Exchange Capacity, [Clay Mineral], [Mica-Like Clays], pH, [Potassium] |
| Cr | [Aluminum/Iron-Oxide Minerals], [Organic Matter], pH, Redox |
| Pb | [Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox |
| Pu | [Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox |
| Rn | None |
| Sr | Cation Exchange Capacity, [Calcium], [Carbonate], pH, [Stable Strontium] |
| Th | [Aluminum/Iron-Oxide Minerals], [Carbonate], [Organic Matter], pH |
| $^3$H | None |
| U | [Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox, [U] |

[1] For groundwaters with low ionic strength and low concentrations of contaminant, chelating agents (*e.g.*, EDTA), and natural organic matter.

[2] Parameters listed in alphabetical order. Square brackets represent concentration.